

Inelastic neutron scattering from antiferromagnetically coupled nearest-neighbor spin pairs in Zn(Mn)O and Zn(Mn)Te

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Abstract

Direct measurements of the nearest-neighbor (NN) antiferromagnetic exchange (J_1) in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ using inelastic neutron scattering from isolated NN spin–spin pairs are reported. The same technique was used for studying $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ at 4 kbar pressure in order to investigate the J_1 change with decreasing spin–spin distance.

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Alloys containing substitutional magnetic metal atoms embedded into a host semiconducting lattice are currently receiving strong interest from the community of researchers working on materials expected to be of potential application in semiconductor spintronics. In particular, much attention is being focused on ZnO-based alloys because it is expected that strongly p-type $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ may become room-temperature ferromagnets due to hole-induced ferromagnetic (FM) exchange between the Mn or Co spins [1,2]. In addition to the hole-induced FM interactions, however, in such alloys there always exist intrinsic *antiferromagnetic* (AFM) interactions between the magnetic spins. These AFM interactions “compete” with the hole-induced FM exchange. In order to make the system ferromagnetic, the FM component should be sufficiently strong to overcome the intrinsic antiferromagnetism. A good knowledge of the AFM interactions is therefore important for understanding the alloy magnetism. To the best of our knowledge, the intrinsic AFM

exchange has not yet been characterized for any ZnO-based diluted magnetic semiconductor (DMS) alloy.

Motivated by this, we have performed neutron scattering experiments in order to determine the AFM parameter J_1 for the nearest-neighbor (NN) Mn^{2+} spins in diluted ($x = 5\%$) $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ alloys. The neutron scattering technique has been used successfully in the past to determine the nearest-neighbor Mn–Mn and Co–Co exchange parameters in ZnTe, ZnSe, and ZnS-based DMS alloys [3,4], but no such studies have yet been performed for the ZnO-based systems.

However, further studies of ZnTe, ZnSe, and ZnS-based DMSs are also worth pursuing because it is an important matter to better understand the intrinsic AFM interactions in the *entire family* of II–VI DMS compounds. In particular, information about the change of J with varying Mn–Mn distance may help to improve the existing theoretical models [5,6]. Such data can be obtained from inelastic neutron scattering measurements at high pressures. In order to test the feasibility of high- P studies, we performed “pilot” experiments on $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$.

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In zinc-blende and wurtzite $\text{Al}_{1-x}\text{Mn}_x\text{B}^{\text{VI}}$ DMS alloys, the Mn atoms are randomly distributed over the fcc or hcp cation sublattices (there are no significant “chemical ordering” effects). The Mn ions may be either “magnetic singlets” (i.e., they have only non-magnetic NNs) or may form NN pairs, triads, etc. The probability that a given ion belongs to a particular cluster type is $P_1 = (1-x)^{12}$ for singlets, $P_2 = 12x(1-x)^{18}$ for pairs, etc. For instance, if $x = 0.05$, 54% of the ions are singlets, 24% are pair members, 4% belong to triads, and the remainder belong to larger clusters. An isolated pair of exchange-coupled Mn^{2+} spins (with $S = 5/2$ each) has a simple scheme of excitation levels of energies $E(S_T) = S_T(S_T + 1)|J|$, where $S_T = 0, 1, 2, \dots, 5$ is the total spin of the pair. Inelastic neutron scattering from such pairs is associated with transitions between adjacent energy levels (the selection rules for the process allow the change of S_T by ± 1). Accordingly, in the scattered spectrum one observes inelastic peaks corresponding to neutron energy gain/loss $\Delta E = \pm 2|J|, \pm 4|J|, \pm 6|J|, \dots$ (for theory details, see Refs. [7,8]).

It should be stressed that in this method the exchange energy is *directly* probed (which is not the case in most other methods of J determination). The peaks from pairs are the dominant feature in the spectra from alloys in the $x \sim 0.05$ concentration range. The triads and other clusters produce much weaker maxima at different positions, so that they do not affect the data accuracy. Essentially, the measurement precision is limited only by the instrumental resolution. Since the scattering is dispersionless, the excitation energies can be obtained from measurements on polycrystalline samples (the use of single-crystal specimens offers certain additional advantages—for details, see, e.g., Ref. [7]).

The experiments were performed at the NIST Center for Neutron Research (Gaithersburg, MD, USA) on the Disk-Chopper Time-of-Flight spectrometer [9] (DCS TOF). The instrument has a good energy resolution in the relevant ΔE range, and it uses a huge array of nearly 1000 He-3 detectors for recording the scattered neutrons in a wide Q -range. This makes the DCS TOF an excellent high-performance tool for studying dispersionless excitations.

The measurements on $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ were performed on a 7 g polycrystalline specimen with $x = 0.05$ prepared by high-temperature sintering [10]. The sample was kept at a constant temperature of 120 K during the measurements.

The $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ sample for high- P studies was obtained by powdering a single-crystal specimen with $x = 0.02$ grown by the Bridgman method. The powder, of approximately 1 cm^3 volume, was placed in a 40 mm cylindrical aluminum cell with 6 mm bore diameter. The cell was placed in a helium cryostat and cooled down to 40 K. Two experimental runs were performed. The first was at ambient pressure to obtain the “reference” data. Then, the cell was pressurized to 4 kbar with helium gas, and the run was repeated.

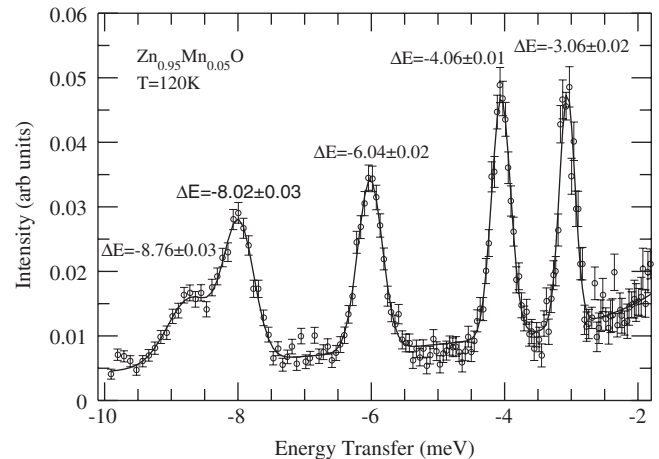


Fig. 1. Inelastic scattering spectrum from $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ at 120 K showing several lines corresponding to transitions between the excited levels of NN spin pairs. The incident neutron energy was 3.55 meV. The negative sign of the energy transfer represents the crystal energy loss. Each data point represents the data summed over the entire range of wavevector transfer covered by the instrument ($0.13\text{--}2.44 \text{ \AA}^{-1}$ for elastic scattering and $1.06\text{--}3.45 \text{ \AA}^{-1}$ for an energy transfer of -8 meV).

An inelastic scattering spectrum obtained from the $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ sample is shown in Fig. 1. To the left of a strong elastic peak (not shown in the plot), one can see a distinct pattern of five maxima (the leftmost two partially overlapping). These peaks clearly correspond to transitions between the excited states of the NN Mn–Mn pairs. The peaks do not occur at regular intervals, so they do not obey the $\Delta E = 2|J|, 4|J|, 6|J|, \dots$ rule outlined above—rather, they indicate that in the system there are spin pairs with two different exchange parameter values, $J_1 = -1.53 \pm 0.02 \text{ meV}$ and $J'_1 = -2.03 \pm 0.02 \text{ meV}$. One conceivable explanation for this is that the difference is associated with deviation from a perfect tetrahedral atomic arrangement in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$. The system has a wurtzite (hexagonal) structure with $c/a = 1.601$ [10], which is a slightly lower value than that for an ideal hcp lattice ($c/a = 1.633$). It means that the distance between the NN Mn–Mn pairs in the basal plane is slightly larger (by 1.26%) than that between the “out-of-plane” NN pairs. As demonstrated by the high-pressure data from $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ (presented below), a change of the ion–ion distance of such magnitude may produce a large change in J_1 .

$\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ is a zinc-blende (cubic) material, so that in this system all NN pairs are equivalent. The J_1 value for $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ ($0.805 \pm 0.003 \text{ meV}$) is known from earlier neutron scattering studies performed on different instruments [3,4]. Inelastic scattering data from $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{Te}$ in a high-pressure cell obtained in the present work are displayed in Fig. 2. For clarity, only the maxima corresponding to the $|S_T = 2\rangle \rightarrow |S_T = 1\rangle$ transition are shown in the plot. The position of the peak measured at atmospheric pressure (3.18 meV) is consistent with the J_1 value known from prior studies. At 4 kbar, the peak is visibly shifted to a higher energy (3.34 meV). The DCS TOF instrument also enables the observation of Bragg

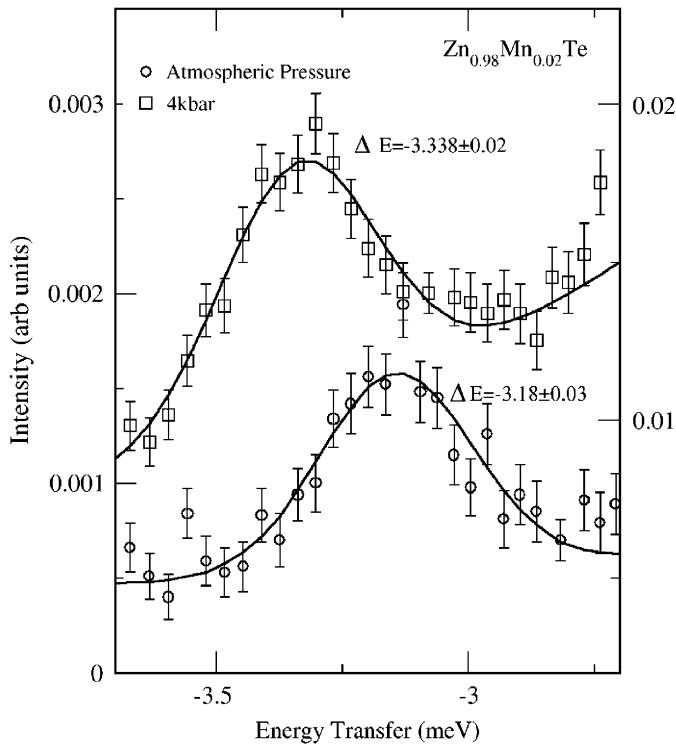


Fig. 2. Inelastic peaks corresponding to the transition of an NN spin pair in $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ from the second excited level ($E = 6|J_1|$) to the first excited level ($E = 2|J_1|$) at ambient pressure and at 4 kbar, plotted in a stretched E scale to emphasize the shift.

scattering. The shift of the (1 1 1) maximum seen at 4 kbar correspond to an NN distance shortening of 0.49%. As shown by the inelastic data, such a shortening leads to a 5% increase of $|J_1|$.

The difference between J'_1 and J''_1 constants seen in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ may arise not only from the difference in ion–ion distance. Another relevant factor in superexchange coupling (which is the principal spin–spin interaction mechanism in the II–VI-based DMS family) is the angle between the cation–anion bonds. These angles are not identical for the “in-plane” and “out-of-plane” NNs in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$. In fact, the bond angles often play a much

greater role than the ion–ion distances. An explanation of the effects seen in the data from $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ may thus require a more sophisticated analysis in which the bond angles would also be taken into consideration.

One more fact that we would like to comment on is that the observed energies of consecutive transitions in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ do not exactly obey the 1:2:3 proportion predicted by the theory. But such a deviation is not uncommon—it is associated with the existence of a higher-order (“biquadratic”) term in the Heisenberg spin–spin interaction Hamiltonian [8].

In summary, inelastic neutron scattering studies of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ have provided direct information about the magnitude of intrinsic AFM interactions in this system. The results of high-pressure experiments on $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ have demonstrated that neutron scattering tools can be successfully used for investigating the dependence of the exchange constants on the spin–spin distance in DMS systems.

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